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Fracture of silica aerogels: An all-atom simulation study

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ABSTRACT

Silica aerogels are highly nano-porous and fragile solids, which exhibit brittle properties under tensile loading. In this work, molecular dynamics simulations with a model size up to 5.07 million atoms have been performed to investigate the effect of the crack length to height ratio on the fracture strength, fracture toughness and strain energy release rate. For a wide range of densities from 295 to 1155 kg m^{-3}, we demonstrate that the fracture toughness and the strain energy release rate at the onset of the crack propagation increase with the crack length to height ratio. Moreover, these fracture properties were found to exhibit a power law dependence on the aerogel density with exponent values of 2.02 ± 0.05 for the fracture toughness and 1.16 ± 0.04 for the strain energy release rate. The investigations presented grant a more comprehensive understanding of the fracture behavior and provide a mechanistic basis for reliable applications of silica aerogels.

1. Introduction

Silica aerogels are amorphous nanoporous materials that exhibit a combination of unique properties such as low thermal conductivity and high surface area [1]. This has made them attractive for a wide spectrum of applications, such as thermal and acoustic insulators, as energy materials, in Knudsen pumps, in aerospace, as shock absorbing materials, and many more [2, 3, 4]. However, in practical applications, where the material is required to carry loads or even maintain structural integrity, silica aerogels become unsuitable due to their brittle nature.

Many recent studies, both experimental [5, 6, 7, 8, 9] and computational ones [10–14], in contemporary research have concentrated on exploring the mechanical properties of silica aerogels. In particular, molecular dynamics (MD) simulations have been exploited to describe mechanical properties of silica aerogels [10–13]. Although preliminary studies had focused on determining certain linear elastic properties of these aerogels [10, 11], more extensive investigations describing the structural evolution under large deformations [12] and reporting on the inelastic effects [13] have been carried out. In our recent work, large-scale simulations of the tensile-compressive behavior of silica aerogels with varying densities were reported [13]. The chosen aerogel model size of 192,000 atoms was created with varying densities by direct expansion of -cristobalite. Due to the large model size, significant improvement in the smoothness of the stress-strain curves in comparison to previous studies [15, 16] was observed. Under tension, the low density aerogels were more ductile while the higher density ones were brittle. On the other hand, under compression, the low density aerogels showed a stress plateau, while the higher density aerogels exhibited an early densification. Furthermore, novel relations were proposed to describe the growth of residual strains, dissipated energy, and the average tangent modulus as functions of applied maximum strain.

As mentioned above, the fragile nature of silica aerogels is a hindrance towards their applicability, and accordingly studying the fracture of these aerogels becomes more relevant and necessary. Howbeit, such investigations remain very few. Experimentally, the fracture toughness has been measured using a single edge notched beam technique in three-point bending [17]. The notches made had a crack length to height ratio a/h between 0.25 and 0.3. It was observed that all stress-strain curves remain linear up to the sudden rupture. Furthermore, the fracture toughness K_{IC} and strain energy release rate G were measured as a function of density. Although K_{IC} was shown to increase with density, oddly G waned. However, the results were accompanied by high error bars. Thus, something conclusive remained hard to attain. This study was followed by a report on the brittle fracture of silica aerogels [9], in which K_{IC} and the crack velocity were investigated not only with increasing density but also with increasing OH content in the gel. It was outlined that the OH content and the porosity along with the pore-size distribution play a crucial role in characterizing the brittle behavior of silica aerogels. The role of pore-size distributions in the mechanical response and in the tensile failure of aerogels has been previously reported [18]. Gonçalves et al. [14] briefly investigated the tensile fracture of silica aerogels via MD simulations. They reported the first signs of tensile failure in silica aerogels at about 20% strains. This

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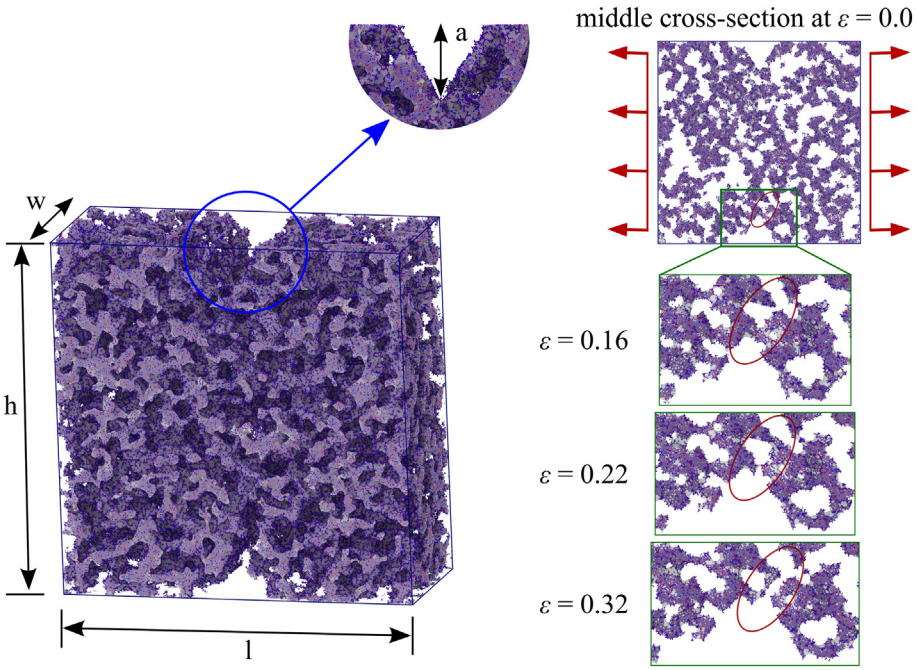

Fig. 1. Schematic representation of an all-atom model and rupture of silica aerogel with a density of 645 kg m^{-3}. a) a (center) denotes the notch depth, while h, l and w represent the height, length and width, respectively. Inset: front view of the v-shaped notch region. b) The snapshots show the fracture of the silica aerogel (failure strain = 0.17). Red arrows indicate that the aerogel was pulled outward under a constant strain rate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

was then qualitatively attributed to the stress drop resulting from the progressive rupture of silica ligaments. In spite of such detailed reports on the mechanical properties of silica aerogels, a thorough investigation on the crack propagation and its effect on the resulting fracture strength, K_{IC}, and G remains to be examined. In this regard, MD simulation has been proven to be a powerful tool to elucidate the crack initiation and propagation in brittle materials at the nanoscale. In particular, it has been successfully applied for a variety of inorganic crystals, such as Si_3N_4 [19], and $CaCO_3$ [20, 21].

Accordingly, in this work, we report on the tensile fracture of silica aerogels using MD simulations, which are based on our previous model [13]. Firstly, the fracture strength is investigated with the increasing crack length to height ratio a/h. Special attention is focused on the fracture properties K_{IC} and G, over a large number of a/h ratios, for a wide range of densities.

2. Methods

MD simulations were performed on silica aerogel models using the program Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [22]. The Vashishta potential [23, 24] was used to model the interatomic interaction for silica (SiO_2), which takes into account the direct atom interaction depending on the distance of separation. This potential also considers the energy associated with the bonding angle and the orientation of three atoms.

The molecular model of silica aerogel was constructed starting with cristobalite atomic coordinates [25]. Initially, periodic boundary conditions were assigned in three mutually perpendicular directions to generate bulk silica. A time step size of 0.5 fs was used for the Velocity-Verlet algorithm in order to solve the equations of motion of the particles. Initially, a random velocity was assigned to the atoms at 7000 K. Subsequently, the sample was quenched to 300 K at 20 K/ps using the NVT (constant volume and constant temperature) ensemble [13, 26, 27], which was followed by the system energy minimization using the conjugate gradient method. Finally, the sample was relaxed to atmospheric conditions (300 K and 1 bar) to generate amorphous silica. The amorphous silica sample was relaxed at 300 K for 7.5 ps followed by an instantaneous expansion to the desired density. The expanded sample was then heated to 3000 K for 50 ps followed by relaxation. Finally, the sample was quenched to 0 K followed by the energy minimization. The porous silica aerogel was formed when the sample is further brought back to the atmospheric conditions. All the heat treatment operations were carried out using the NVT ensemble except for the relaxation, which was performed using the NPT (isothermal–isobaric) ensemble. The last frames were used to create notched models. The range of the densities considered in this study was from 295 to 1155 kg m^{-3}. Silica aerogels are characterized by a very complex structure, wherein the atoms are arranged randomly. Therefore, to avoid the model dependent mechanical properties in MD simulations, four different silica aerogel models were independently created, and the resultant properties were analyzed together. In Section 3 (Figs. 2, 4, 5, 6), the variation in their results was determined based on the standard error deviation, and is accordingly elucidated.

The separated distance between two atoms or the bond length can be computed using the radial distribution function (RDF) denoted by $g(r)$. In the present work, for Si—Si, Si—O and O—O the pair distances were calculated as 3.066 Å, 1.609 Å and 2.626 Å, respectively. These pair distances show good agreement with the simulation [15] and experimental [23] studies reported in the literature. A detailed discussion of the RDF is included in the Supplementary material.

For the fracture simulations, double-notched silica aerogel models were built (Fig. 1). The periodic vector through the width w was considered, resulting in fracture models of infinite length along w-direction. Then, the v-shaped notches were introduced by removing atoms. Afterwards, the atomic structure was relaxed up to 100 ps using the NVE (constant volume constant internal energy) ensemble. A constant strain rate of 0.004 ps^{-1} was applied to both ends of the model (the strain rate sensitivity analysis was studied in our previous work [13]).

Due to the applied external loading, mechanical stresses concentrate at the flaw tip. As the stress reaches a critical value σ_f, the so-called rupture strength, the stress at the tip is high enough to overcome the cohesive energy among molecules, forcing the material to separate into two surfaces. The energy-based criterion for fracture of brittle materials was proposed by Griffith [28] with the rupture strength as

$$\sigma_f = \frac{1}{\alpha}\left[\frac{2E\gamma}{\pi a}\right]^{1/2} \quad (1)$$

where a is the notch depth, γ is the surface energy, E is Young's modulus, and α is a geometry correction factor. For the double edge notched tension of a semi-infinite model with notch depth a and height h, α was given by [29].